AFATL-TR-82-32

Ambient Moisture Effects and Closed Vessel Studies of Gun Propellant Combustion

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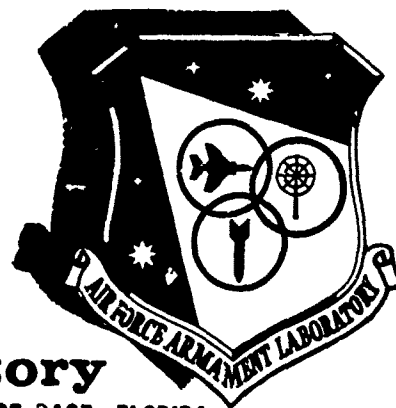T W Shiver

BALLISTICS BRANCH
DIRECT FIRE WEAPONS DIVISION

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    This report covers several topics in the field of solid gun propellant combustion. They include: (1) mass spectrometry to experimentally define the gas products of gun propellant combustion and correlate these experimental results with theoretical predictions; (2) the use of closed combustion bomb pressurization rates to extract solid propellant linear burning rate values is discussed, and correlations with strand burner data are considered; (3) the effects of moisture adsorption on solid propellant combustion rates and energy are experimentally defined, and (4) a reference section of solid propellant

20. ABSTRACT (CONCLUDED)

combustion product specific heat ratio values is provided.

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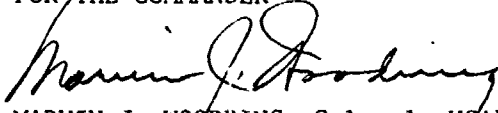Special

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PREFACE

This report has been generated under the requirements of in-house work units 2560-08-19 and 2560-08-20, which sponsor on-going evaluation of gun propellant performance, and continuing investigations into the nature of the physics and thermodynamics, which control gun propellant combustion, and thereby the efficiency of the aircraft cannon ammunition systems.

The presented analytic and experimental data were generated at the Interior Ballistics Laboratory of the Direct Fire Weapons Division, Air Force Armament Laboratory during the period from February 1981 to March 1982.

The Public Affairs Office has reviewed this report, and it is releasable to the National Technical Information Service (NTIS), where it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication.

FOR THE COMMANDER

MARVIN J. WOODRING, Colonel, USAF
Chief, Direct Fire Weapons Division

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SECTION I

INTRODUCTION

This report describes the procedures and results of some aspects of temperature effects analysis and closed vessel in-house gun propellant research and development conducted in the Interior Ballistic Laboratory of the Air Force Armament Laboratory.

The initial two topics which will be discussed are somewhat disparate and related only through the fact that both are closed vessel approaches to analyze the combustion properties of gun propellants. The first is a combustion bomb mass spectrometer assembly in which small (3-gram) samples of gun propellant are burned and immediately fed into a time-of-flight mass spectrometer for combustion product analysis. These approaches and results will be discussed in Section II.

The second technique which will be covered is the use of a closed combustion bomb to extract linear burning rates. The approach historically used at Eglin and described in Reference 1 is that of the very high pressure prepressurized linear strand burner, as opposed to a closed combustion bomb. The closed vessel work was undertaken as part of a JANNAF work shop, and the experimental results acquired were surprisingly consistent. These results and the mathematical data extraction used are presented in Section III.

The third area which will be addressed is that of ambient moisture effects on solid propellant combustion performance. This topic arose from occasional drastic experimental performance degradation in the GAU-8 gun from a given lot of propellant of known baseline performance.

A final short reference section is included to provide specific heat ratio values for the typical gun propellant combustion specie constituent gases as a function of temperature and pressure. This data is frequently required for various interior ballistic computations and is not conveniently available in any single reference.

SECTION II

COMBUSTION PRODUCT ANALYSIS BY MASS SPECTROMETRY

Various types of mass spectrometers have been available to the combustion community for some time and the limitations applying to their use as a tool to quantitatively analyze gun propellant equilibrium combustion products are well appreciated. The primary drawbacks are that (1) two of the main combustion products, CO and N_2, fall at the same molecular weight of 28; (2) water will immediately condense on the relatively cool bomb walls and be virtually undetectable; and (3) hydrogen tends to be absorbed or adsorbed by almost everything in the sampling system and is difficult to handle quantitatively. Also, the relative violence of the sampling process in the mass spectrometer results in the decomposition of a portion of the formed species. In standard test practice, an electron beam energy of 70 electron volts is used to knock an electron off the molecules to be sampled. This can split, for example, a molecule such as CH_4 into CH_3, CH_2, and CH; or CO into C and O. Alternatively, the electron beam may knock two electrons rather than one off CO_2 at mass unit 44, with the result, that it appears to have a mass unit of 22. Due to these drawbacks, researchers typically tend to rely on theoretical thermochemical combustion specie computations, such as that described in Reference 2, rather than experimental analysis.

The persistent problems with the A-10 aircraft ingesting GAU-8 muzzle gases lent impetus, however, to a program oriented toward determining what could be learned from an experimental examination of the combustion of various propellant types and their resultant combustion gas species. The types investigated, along with their theoretical free energy mole fraction combustion products, are given on Table 1. The propellants consist of a single base, a double base, and a nitramine formulation. The theoretical mole fraction values were determined by means of a NASA Lewis free-energy program modified for constant volume applications (Reference 2). The mole fraction values labeled "hot" are effectively the gases expected at combustion chamber conditions while the values labeled "cold" are the resultant theoretical values subsequent to an expansion to ambient pressure and temperature conditions.

Experimentally, the propellant was burned in a Paar bomb located directly at the input of a CVC MA-2, time-of-flight mass spectrometer (Figure 1). The

TABLE 1. THEORETICAL MOLE FRACTIONS

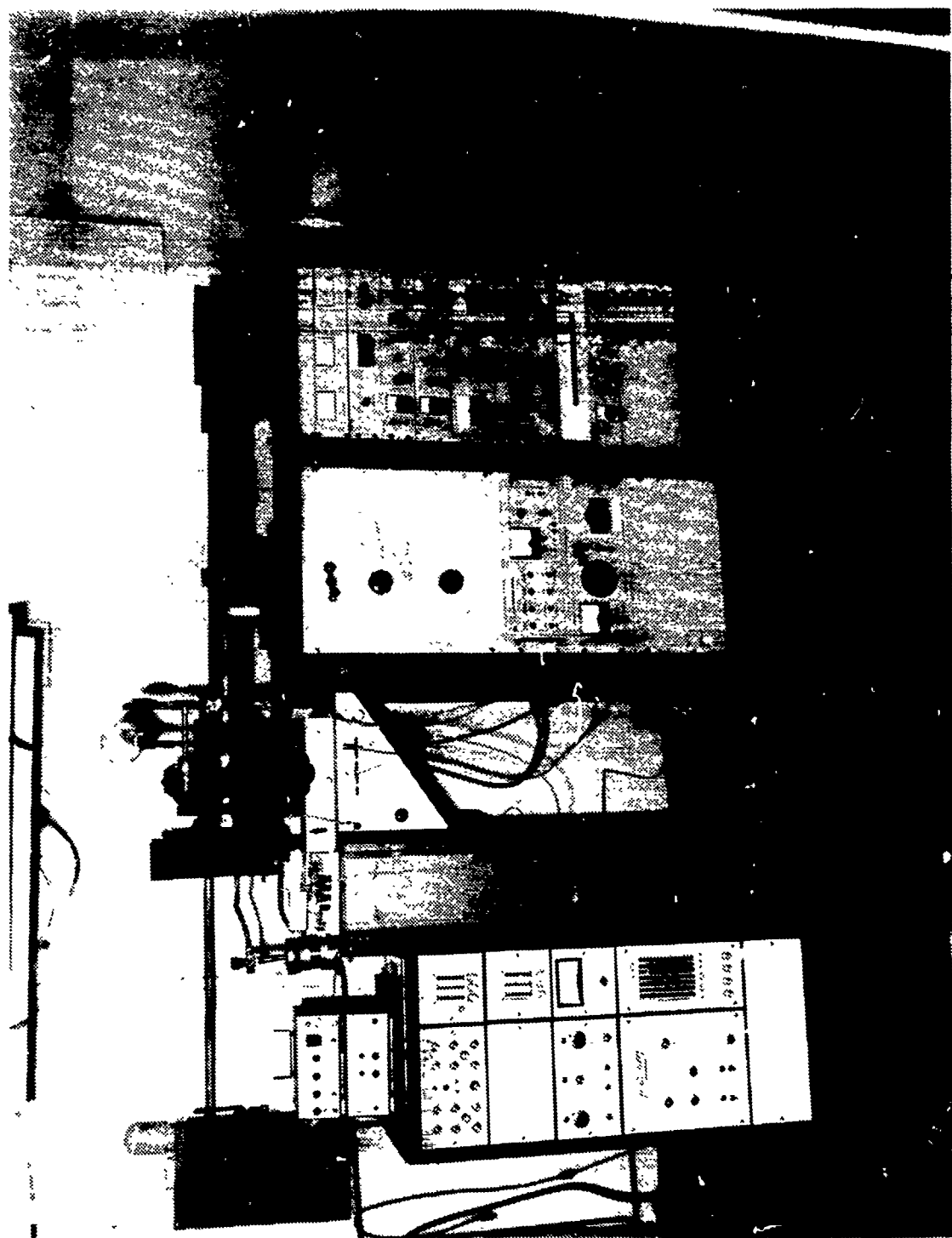| SPECIE	MOLECULAR WEIGHT	SINGLE BASE		DOUBLE BASE		NITRAMINE	
		HOT	COLD	HOT	COLD	HOT	COLD
CO	28	45	36	45	36	27	17
CO_2	44	10	19	9	19	3	10
H_2	2	15	22	17	23	31	28
H_2O	18	19	11	18	10	14	11
N_2	28	11	11	10	11	26	28
CH_4	16	0	0	0	0	0	4

Figure 1. Time-of-Flight Mass Spectrometer

"hot" data were repeatedly sampled within one minute of the firing. The cold data were generated by bleeding the Paar bomb pressure to 25 psig and sampled after a 12-minute cooling cycle.

These type formulations were experimentally evaluated with the basic results as shown on Figures 4 through 6.

Prior to a discussion of the correlation of species between theory and experiment, it is useful to discuss how the time-of-flight mass spectrometer is quantitatively calibrated. This process is somewhat Edisonian and largely accomplished through the use of calibration gases of known specie percentages.

HYDROGEN. In general, the detectors of the type used in the equipment available for this program are less sensitive to hydrogen than the higher mass unit gases. To determine the sensitivity factor, a known mixture of 98 percent air and 2 percent hydrogen is introduced into the machine. As only 25.1 percent of the hydrogen known to have been introduced is detected, a factor of 3.99 is used to enhance the detected level for subsequent experimental testing.

WATER. Subsequent to propellant combustion in the bomb, the gas phase moisture will immediately condense on the relatively cooler walls of the bomb. Careful recovery of this water from the bomb walls and end plates typically results in values of 11 percent by weight or 15 percent by mole fraction of water from the combustion process. This is virtually 100 percent of the theoretical water formed during combustion. Thus, on the computer data reduction, a water correction factor is inserted to correct the mole fraction output results for this water which does not enter the mass spectrometer sampling system.

MOLECULAR FRACTURE. Due to the violent nature of the electron beam impact used to charge the gas particle to be sampled, a fixed percentage of each type of gas encountered will be broken into fragments. For a given electron beam intensity, in this case 70 eV, the fractions remain constant and are given below. These fractions are determined by repeatedly sampling calibration gases of well known composition. For the fragment fractions given, the numbers are references to 100 percent for the peak of the sampled gas itself. It should be remembered that these values are system and energy level specific.

CO 100% CO
   4% C
   1% O

CO_2	100% CO_2
	12% O
	11% CO
	6% C
N_2	100% N_2
	6% N
CH_4	100% CH_4
	67% CH_3
	13% CH_2
	7% CH
	2% C

From the above, it is seen that molecules such as CO_2 and CH_4 will fragment very badly during the sampling process. The fragmentation fraction of N_2 allows the quantitative separation of the CO - N_2 peak at mass unit 28. The component due to N_2 at AMU 28 will be 16.5 times the value at AMU 14. The remainder at this mass unit will then be CO.

DATA REDUCTION. The raw data from the mass spectrometer, which provides typical initial output as per Figure 2, is fed into a Tektronix 4054 Data Processor. Processing of data is conducted in accordance with the discussion in the paragraphs above. The hydrogen detection level is enhanced, a manually recovered water factor is included, the N_2 - CO ratio is determined from the N fraction at AMU 14, and compensation is made for the known fracturing of molecules by the electron beam energy. Figure 2 consists of raw relative specie data for a single base nitrocellulose propellant. It is seen that almost 85 percent of the output is located at the peaks of 44 (CO_2) and 28 (CO, N_2). This data, along with those pertaining to the minor constituent species, is then machine processed by the techniques discussed above to provide an output as per Figure 3. The logic flow is to first split the mass peak at 28 into components using the measured intensity values. The hydrogen sensitivity factor and molecular fracture percentages are accounted for in the corrected intensity column. Finally, the overall percentage numbers are again modified to account for the manually recovered water from the combustion bomb interior.

SAMPLE: M-10
CONDITIONS: 3 GMS @ 50 PSI
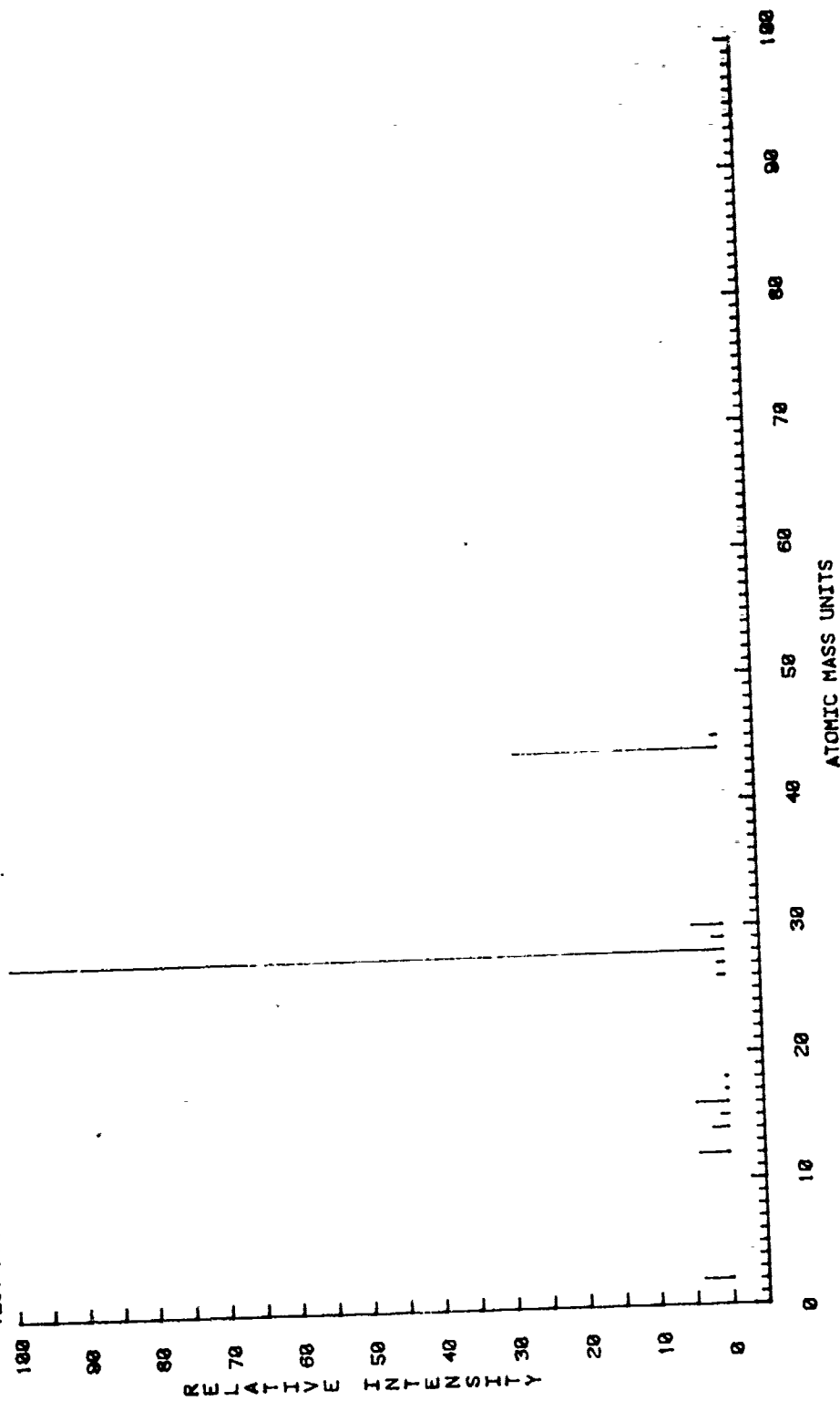DATE: 15 JAN 82
TEST NO.: 2

ATOMIC MASS UNITS

RELATIVE INTENSITY

Figure 2. Raw Data: Single Bass Propellant Combustion Specie Mass Fractions

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SAMPLE: M-10
CONDITIONS: 3 GMS @ 50 PSI
DATE: 15 JAN 82
TEST NO.: 2

HYDROGEN SENSITIVITY FACTOR: 3.987

WATER CORRECTION: 0.15 %

MASS UNIT	MEASURED INTENSITY	MEASURED PERCENT	CORRECTED INTENSITY	CORRECTED PERCENT	CORRECTED PERCENT/H2O
2	13.00	2.55	51.83	9.78	8.31
12	14.00	2.74	0.44	0.08	0.07
14	7.00	1.49	0.00	0.00	0.00
15	3.20	0.63	3.20	0.60	0.51
16	15.00	2.94	3.66	0.69	0.59
17	1.00	0.20	1.00	0.19	0.16
18	1.00	0.20	1.00	0.19	15.16
26	3.00	0.59	3.00	0.57	0.48
27	3.00	0.59	3.00	0.57	0.48
28	335.00	65.27	330.49	62.35	52.99
29	5.00	0.98	5.00	0.94	0.80
30	14.50	2.84	14.50	2.74	2.33
44	94.50	18.52	118.57	20.86	17.73
45	2.40	0.47	2.40	0.45	0.38

2 ... H_2		18 ... H_2O
12 ... C		26 ... CN
13 ... CH		27 ... HCN
14 ... N, CH_2		28 ... CO, N_2
15 ... CH_3, HN		29 ... HCO
16 ... O, CH_4		30 ... NO
17 ... OH, NH_3		44 ... CO_2

REMARKS

1. OF THE MEASURED 65.27 PERCENT AT AMU 28
   24.58 % IS NITROGEN
   40.69 % IS CARBON MONOXIDE

2. OF THE CORRECTED 62.35 PERCENT AT AMU 28
   23.66 % IS NITROGEN
   38.69 % IS CARBON MONOXIDE

3. OF THE H_2O CORRECTED 52.99 PERCENT AT AMU 28
   20.11 % IS NITROGEN
   32.89 % IS CARBON MONOXIDE

Figure 3.   Computer Output: Single Base Propellant Combustion
Specie Mass Fractions

Hot and cold theoretical and experimental combustion specie results for a single base, double base, and nitramine gun propellant are contained on Figures 4, 5, and 6, respectively. Some general results for the three cases are immediately apparent. In all cases, experimental results for hydrogen are lower than theoretically predicted. This is no doubt due to adsorption of a portion of the hydrogen onto bomb parts prior to introduction into the spectrometer sampling system. The experimental water recovered is consistent at about 15 percent irrespective of the sampling temperature. This would be expected as the combustion water probably immediately condenses on the cooler metal bomb walls. Virtually all the water formed during combustion is recovered from the bomb and does not enter the spectrometer sampling system. This is not the case for moisture in the air as humidity, which is very readily detected during routine system background checks.

For the N_2 specie, experimental results tend to be consistently higher than theoretical predictions, while for CO the experimental values are consistently lower than the free energy predictions. This is due to a biased shred-out of the mass peak at 28, which probably occurs due to the existence of other fragments at mass 14 that were not there during the calibration process.

In conclusion, it can be stated that the mass spectrometer is a less than ideal tool for specie verification. The physics and thermodynamics of the inlet process and the violent dynamics of the sampling process result in a nested array of correction factors that somewhat tarnish the scientific elegance of the experiment. Nonetheless, the data presented on Figures 4, 5, and 6 are suitable to determine the general quantity and type of combustion products emitted during cannon firing and that are likely to accumulate in an onboard gun-firing bay.
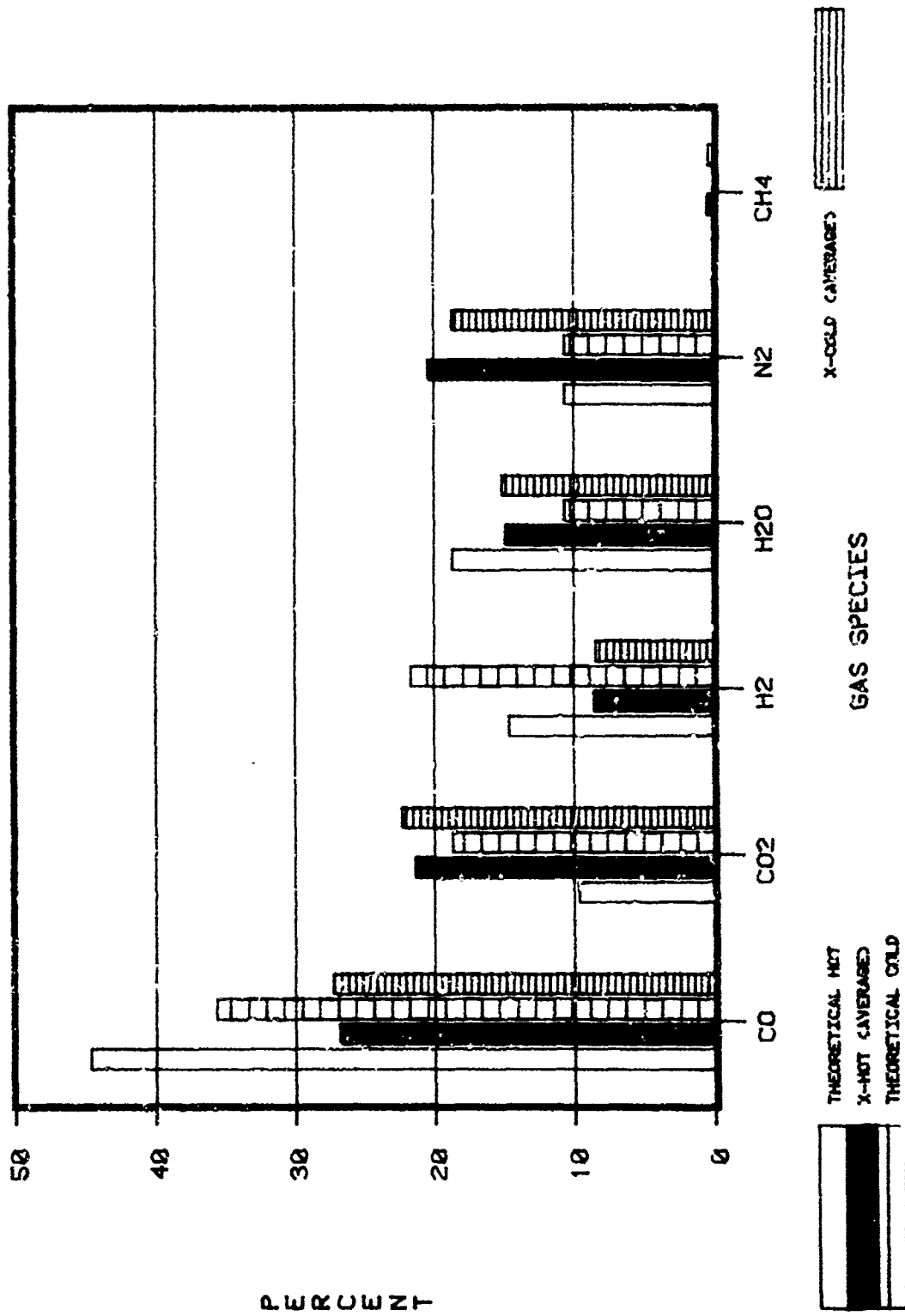
Figure 4. Single Base Propellant Combustion Products

DOUBLE BASE (AVERAGE)
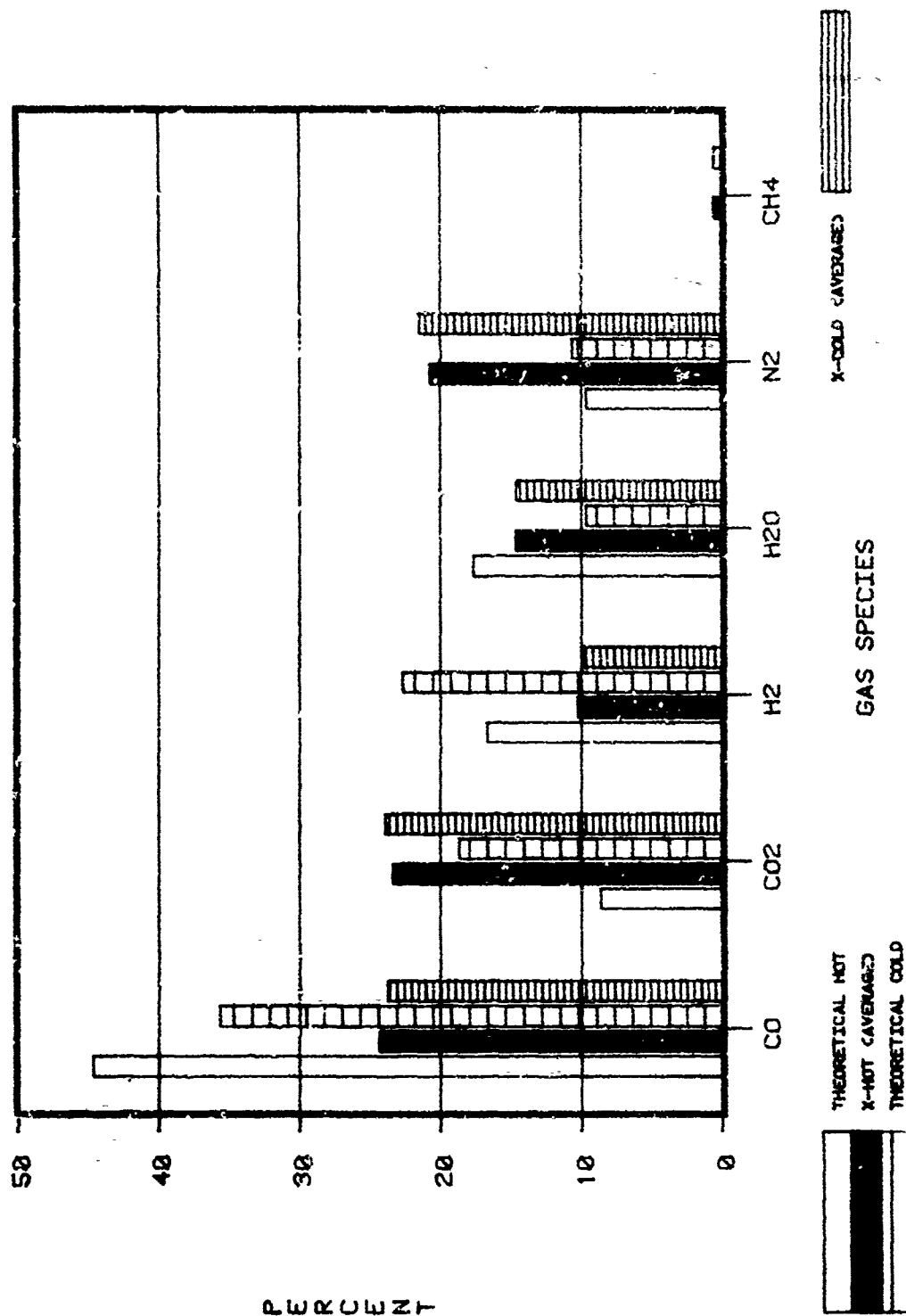
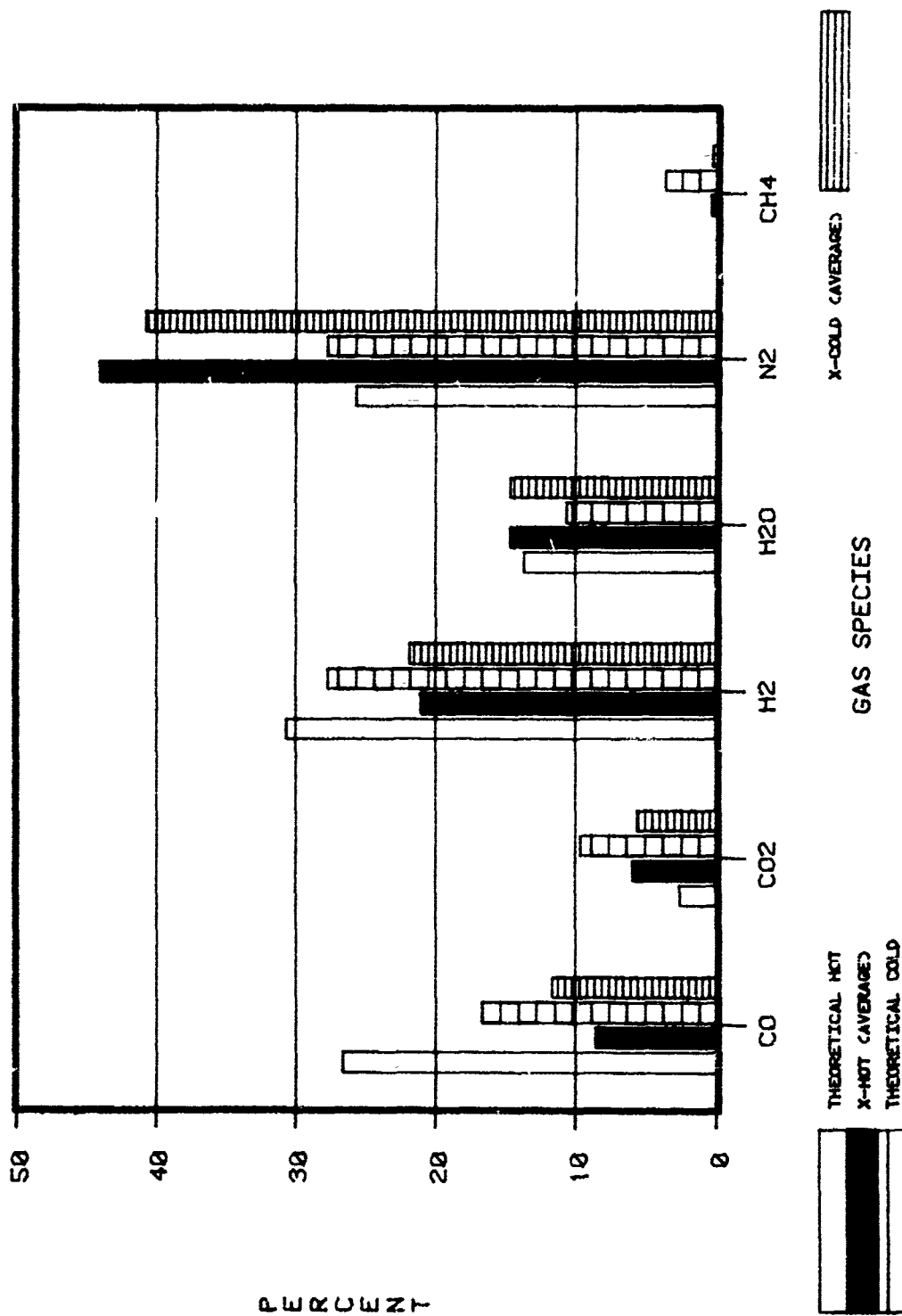Figure 5. Double Base Propellant Combustion Products

Figure 6. Nitramine Propellant Combustion Products

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SECTION III

CLOSED BOMB BURNING RATE ANALYSIS

The technique which has traditionally been used at Eglin to determine linear burning rates of advanced and conventional gun propellants is that of the pre-pressurized strand burner. This is a high pressure (50,000 psi) variant of the standard rocket industry Crawford bomb. However, due to the high initial capital costs and intensive maintenance required with multiple stage intensifier high pressure strand burners, much of the gun propellant community has, over the years, attempted to extract burning rates from closed vessel combustion bombs.

The closed bomb approach uses a much simpler experimental set-up but requires complex computer processing of pressurization rate data to generate the desired burning rates. A JANNAF committee has been established for some time to coordinate and correlate the approaches from various government and industry laboratories for a solution of the burning rate determination problem. The purpose of this report is to describe the methodology used at Eglin to extract linear burning rates from bomb pressurization data.

Closed impetus bombs have been available to the propellant industry for many years. The type used at Eglin is a 90-cubic centimeter Technoproducts model as described in Reference 3. The advantage of using this device is a very rapid load, fire, and turnaround capability. The disadvantage is that main seal leakage problems start at pressures around 30,000 psi and consequently in routine usage, the operating pressure of the bomb is held to a relatively low 25,000 psi. For impetus calculation, the bomb operation is quite simple and uses only the final peak pressure and a Nobel-Abel equation of state

$$P(V-\eta) = nRT \qquad (1)$$

where $RT = F\rho$; the impetus, and

$$n = C\omega \text{ charge mass, with}$$

$$\eta = C\omega \cdot \eta' \text{ is specific covolume}$$

This covolume η' has a typical value of 29 cubic inches/pound for gun propellants and accounts for the fact that combustion products are not mass points but rather take up a finite volume of the available combustion chamber.

Thus, to express impetus in the customary units of foot/pounds, Equation (1) becomes

$$F = \frac{P(V-\eta)}{12 \ C\omega} \qquad (2)$$

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From Equation (1), it is also seen

$$dn/dt \sim dP/dt$$

Thus, from the time rate of bomb pressurization, one can extract a gassification rate dn/dt. Also if

$$dn/dt = rS_\beta C_\rho \qquad (3)$$

the gassification rate, as a function of pressure, will lead to a linear burning rate r as a function of pressure, given that S_β is at all times accurately known. The basic problem associated with determination of linear burning rates from closed vessel pressurization data is that S_β may not be fixed or adequately expressed analytically and severe bias errors may arise from only the gassification rate being experimentally measured.

Figure 7 is a typical closed bomb pressure versus time profile acquired from the Technoproducts bomb using a Kistler 607C gauge fed into a Nicolet Explorer III Digital storage oscilloscope. These results are not typical, only to the extent that they contain 60 microseconds of bad data due to either momentary guage or scope analog-to-digital converter failure.

As the rate of pressurization is the parameter of primary interest, the data must be differentiated either directly numerically or a polynominal fitted and then the polynominal analytically differentiated. Only the center part of the pressure rise curve can be utilized. The points to the left of the start line on Figure 7 cannot be used as this area is part of the ignition cycle rather than linear combustion, and all faces of the bulk grain burning surface have not yet been ignited. Attempted data reduction in this regime will lead to certain error, as would attempts to process data lying past that portion of the curve to the right of the stop line, at which point propellant grains have started to fracture and/or burn out.

As data is acquired every 20 microseconds, the approximately 2.5 milliseconds of data between the start and stop fiducial values on Figure 7 are represented by 126 discrete values. As direct numerical differentiation has proven in practice to be erratic and highly noisy, the AFATL approach has been to least squares fit all points within the selected range to a 5-degree polynomial per techniques in Reference 4. The detailed computer output includes a series of constants A_1 to A_6 giving a best fit to the pressure time data. In this approach,

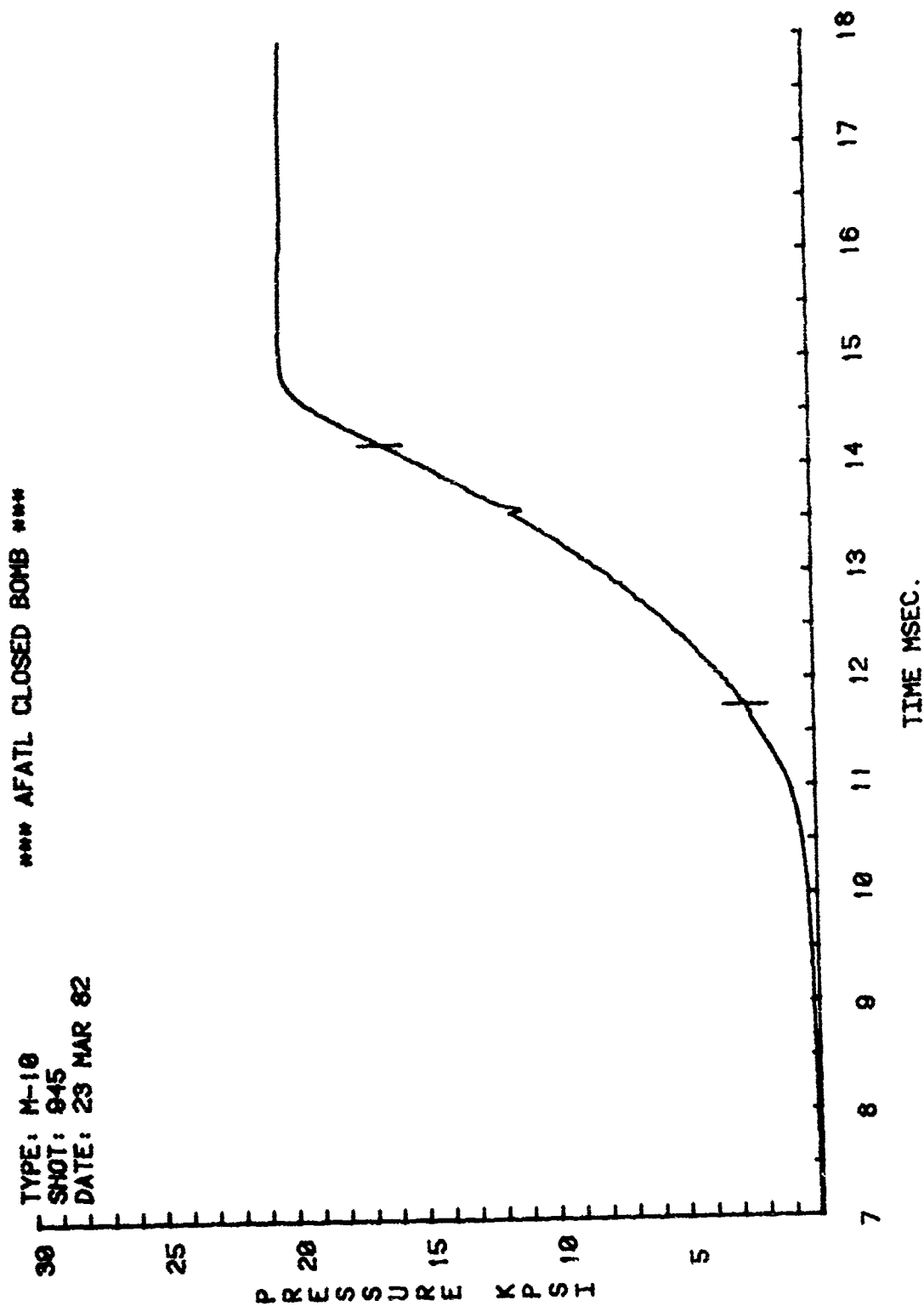$$P = A_1 + A_2 t + A_3 t^2 + A_4 t^3 + A_5 t^4 + A_6 t^5; \qquad (4)$$

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Figure 7. Typical Closed Bomb Pressure-Time Trace

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then,

$$dP/dt = A_2 + 2A_3t + 3A_4t^2 + 4A_5t^3 + 5A_6t^4 \cdot \qquad (5)$$

The nature of this type fit to the data is shown on Figure 8 with the equation provided by Equation (4) compared to the 126 points of discrete data. It is seen that the fit is outstandingly nice; in addition, a major advantage of this approach is that if a few spurious points such as those centered at 13.6 milliseconds exist, they will be all overwhelmed by the mass of "good" data contained in the other 123 points. The analytic differential of Equation (4) is Equation (5) which with Equation (3) and assuming the burning surface is either fixed or known, provides a burning rate per Figure 9. This data is for M-10 which was the subject of a JANNAF Round Robin evaluation of closed vessel and strand burner techniques in various laboratories. AFATL strand burner and closed vessel burning rate values as well as closed vessel results from other laboratories are presented on Figure 10.

Figure 10 serves as a good illustrative example of some of the limitations of using a closed bomb for burning rate data extraction. It is seen that the results of three laboratories show very low burning rates for M-10 at 1,000 psi which subsequently rapidly rise to the 2,500 psi range and then level out. This is a clear indication that, in this range, the ignition cycle has not yet been completed. Clearly what has been measured in this region by the time differential of the pressure data is not a burning rate but rather an ignition flame spread phenomenon.

The data on Figure 10 represent single perforate propellant which is also the simplest case to deal with, as the burning surface can be considered to be relatively constant (per Reference 6). For a seven-perforate propellant, the burning surface is not constant but rather progressive, and resort must be made to either geometrical arguments or closed form "form functions" which are described in detail in Reference 7. Whichever approach is utilized, the burning surface data becomes invalid at the point of web burnout to slivers. Irrespective of any sort of painstaking analysis at this point, the inherent natures of manufacturing and fracturing irregularity render the process fundamentally non-analytic.

An additional problem that arises when dealing with seven-perforate propellant is that of what initial burning surface with which to start computations.
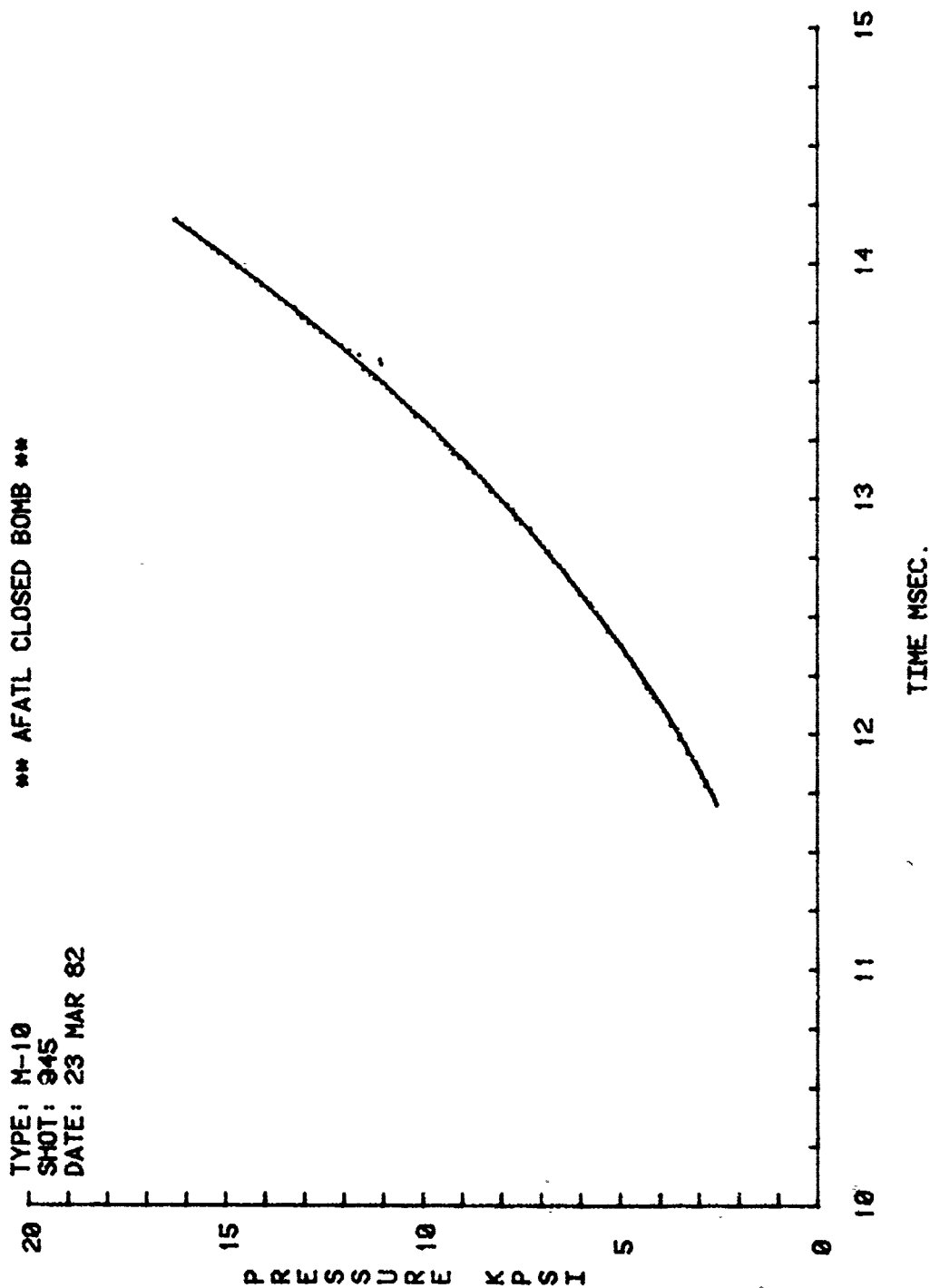
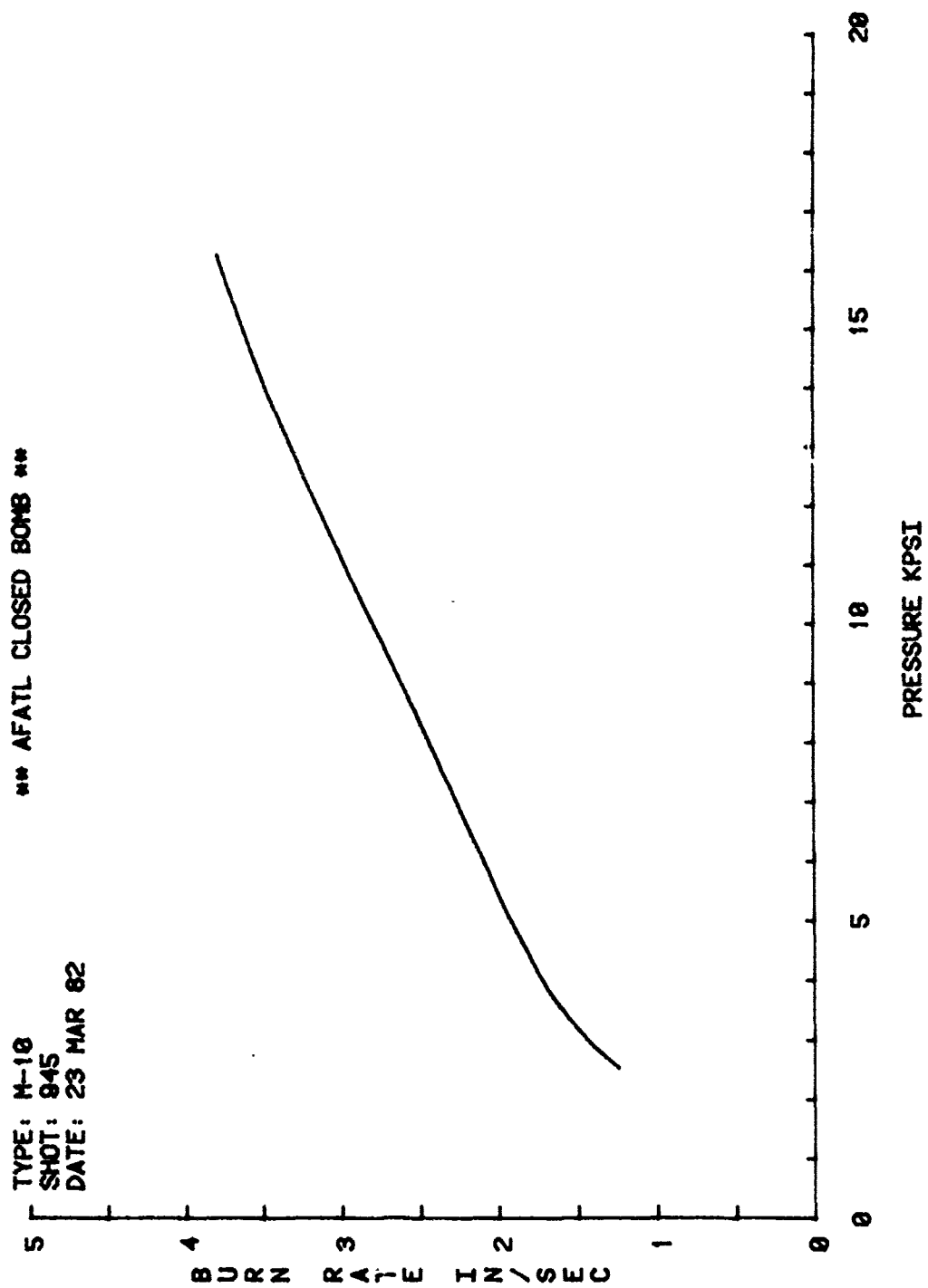Figure 8. Polynominal Fit to Experimental Pressurization Data

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Figure 9. Closed Bomb Burning Rate from Differential of Pressurization Data
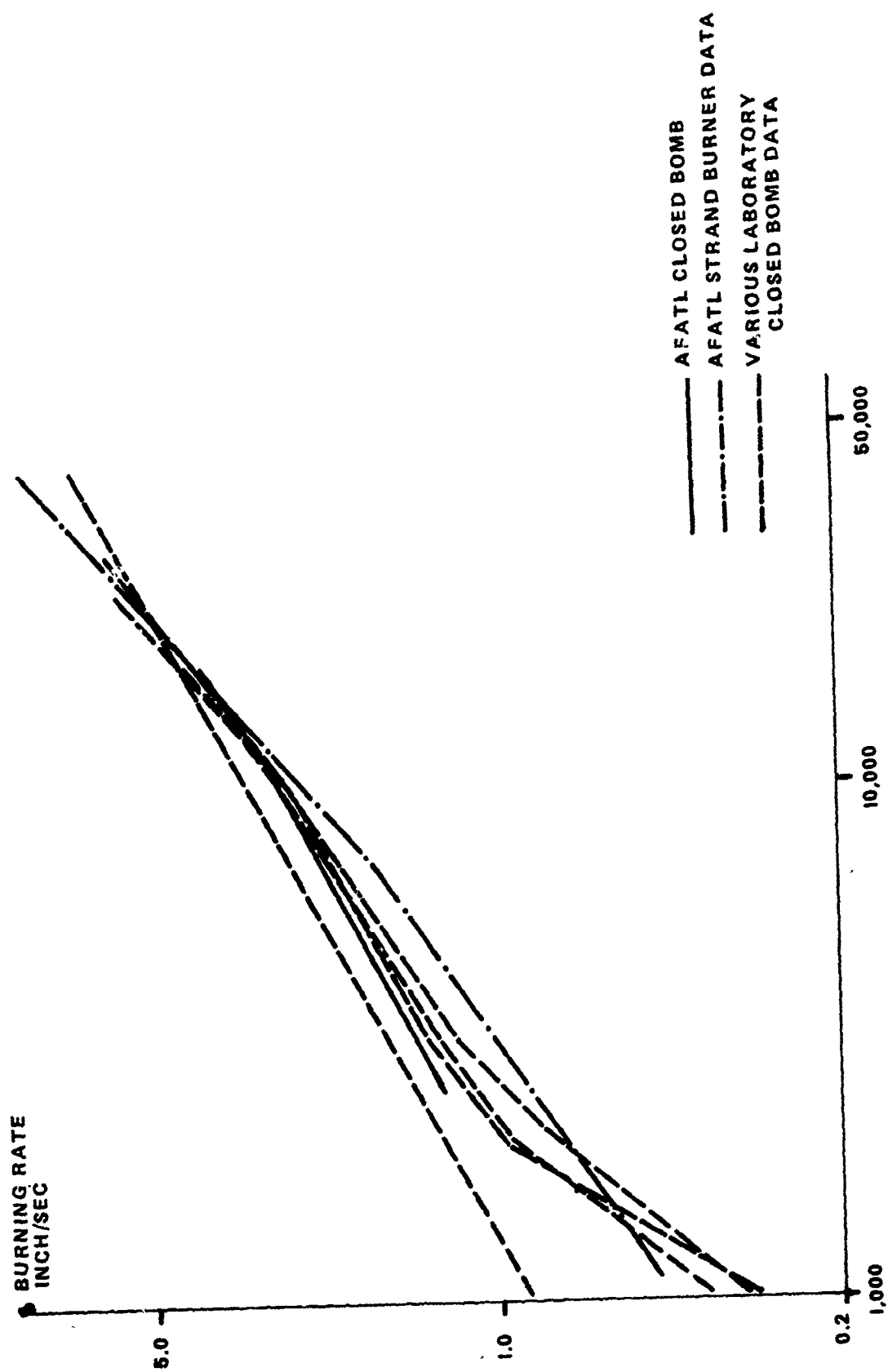
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Figure 10. Experimental Burning Rates from Various Laboratories

This is particularly true if the mathematical differential is not initiated at the start of burning, which, in general, it is not, but rather subsequent to the ignition transient. The manner in which this is handled at the Air Force Armament Laboratory (AFATL) is to assume linear mass consumption as a function of start pressure to peak pressure and enter the form function relationship at the appropriate mass consumed pressure ratio point. This is a reasonable approximation but again can provide bias errors.

An additional consideration for which compensation is generally made is that of heat loss to the walls of the bomb. Using the AFATL bomb, this is a surprisingly small correction, as the impetus efficiency tends to run in excess of 97 percent. The procedure used to make this minor heat loss correction is to increment all burning rates by a factor determined by a ratio of the inverse of the experimental efficiency. In this case

$$r' = r/.97 = 1.031r$$

This can be thought of as a distributed or PDOT heat loss correction approach.

The plot of the burning rates from the various techniques and differing laboratories given on Figure 10 shows a high degree of scatter below 10,000 psi but a reasonable convergence above that point. As the main working pressures in a typical gun are above 10,000 psi and the lower regime is largely in the ignition transient of the ballistic cycle, closed bomb burning rate data is of some utility for interior ballistic calculations. The primary approach that will continue to be used at Eglin for burning rate determination is that of the linear strand burner. For those organizations without access to this type equipment and who, by necessity, must resort to closed bomb burning rate data extraction, the AFATL programs are available programmed in either Basic or Fortran upon application to AFATL/DLDL.

SECTION IV

MOISTURE EFFECTS ON PROPELLANT COMBUSTION

The normal climate at Eglin Air Force Base is exceptionally humid, with
the result that stored gun propellant can often be exposed to simultaneously
high levels of high temperature and humidity for extended periods. Often,
locally stored Class B propellant cannot be protected in hermetically sealed
bulk munition cans without reclassification as Class A, resulting in storage
compatibility problems. This normally results in bulk propellant being locally
stored in vented containers.

It has previously been reported that the GAU-8 gun, with its plastic
rotating bands, showed a high degree of performance variation with very slight
changes in barrel chamber design (Reference 8). Performance of a given lot of
locally loaded propellant, in the same chamber, has also experimentally been
seen to slowly degrade with time. It was intuitively postulated that the per-
formance decrease was due to ambient humidity effects on the nitrocellulose
propellant.

Recently an experimental firing program has been conducted at AFATL to
quantitatively define the effect of adsorbed moisture on this double base gun
propellant in the GAU-8 cartridge. All shots were fired with a 428-gram pro-
jectile with a 154-gram propellant charge from the same Mann barrel. Each
listed data point consists of an average of 5 firings at the specified time
of subsequent drying.

The double base propellant used for this test was taken from a single lot
at ambient storage. It was spread on open trays and exposed in an environmental
chamber to 95°F and 95 percent relative humidity for a period of 8 days. From
tray to tray the adsorbed weight of water, due to this treatment, was a very
uniform 1.13 percent.

The propellant was then dried at 110°F in a forced air oven at virtually
0 percent relative humidity (RH). Gun firings were conducted after 0, 1, 2, 4,
8, 24, and 67 hours of drying. The results are plotted on Figures 11 for
chamber pressure versus conditioning time and Figure 12 for muzzle velocity
versus conditioning time. It is immediately seen that the effect of adsorbed
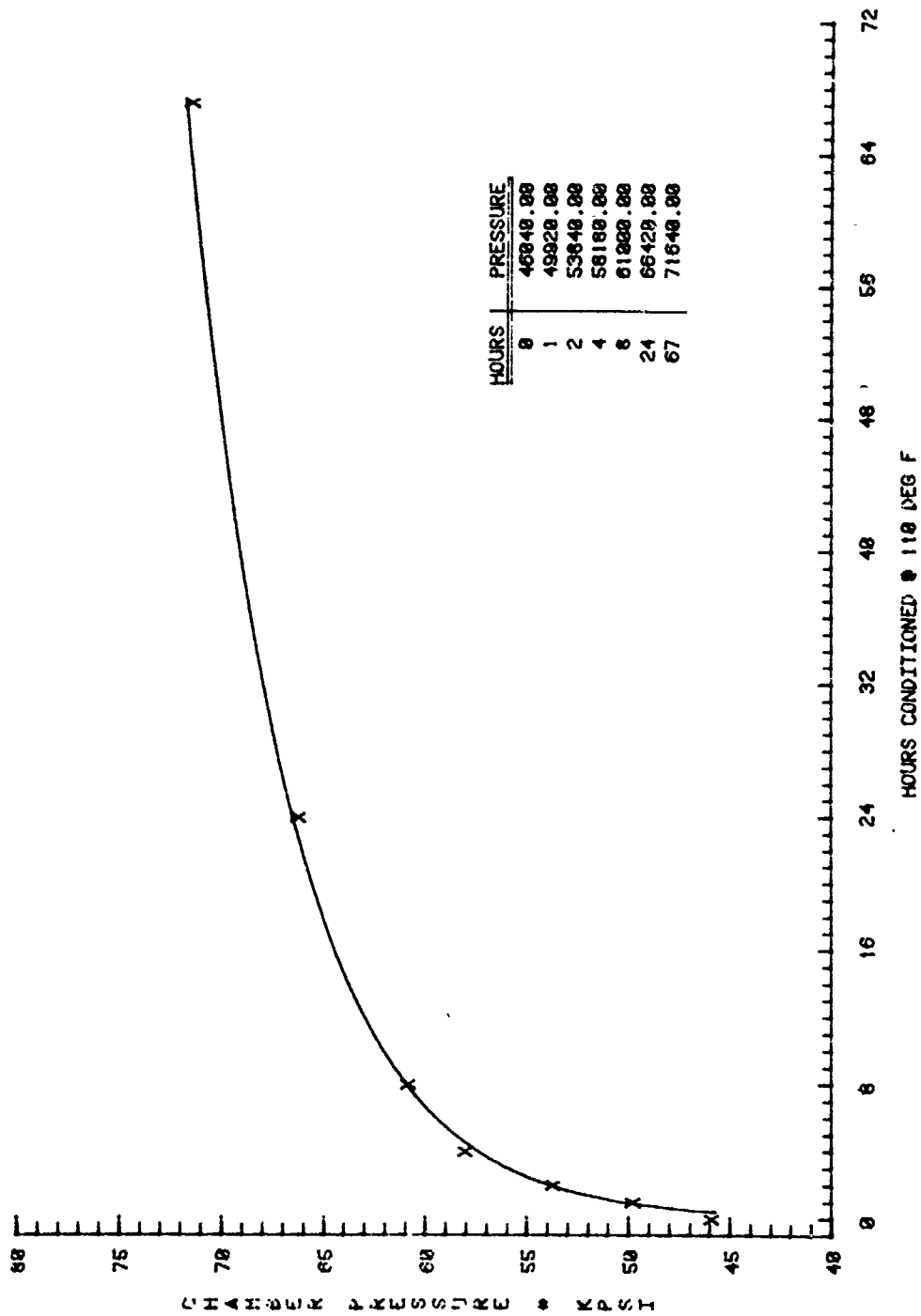moisture on performance is phenomenally strong.

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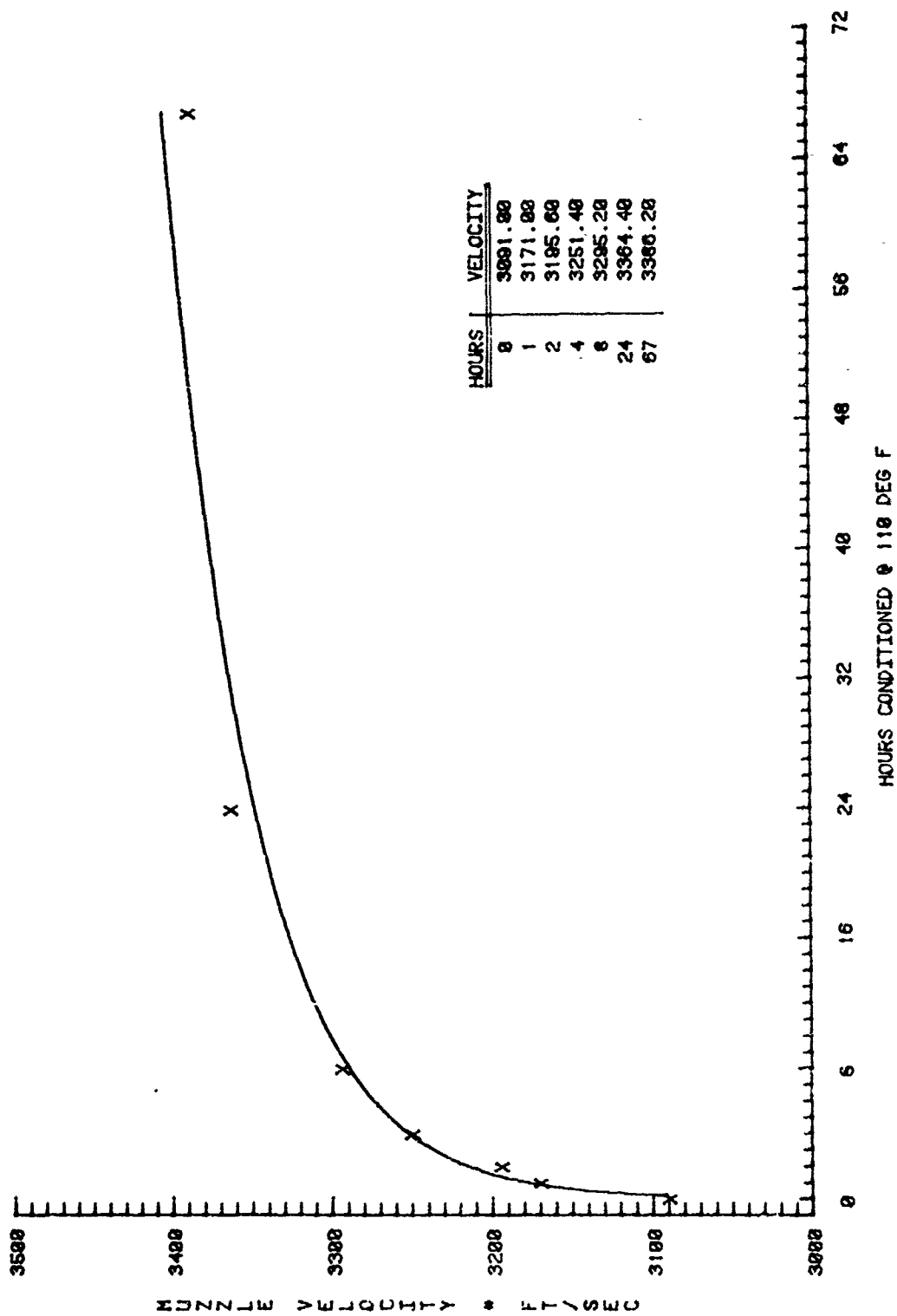Figure 11. Peak Pressure Versus Conditioning Time

HOURS	PRESSURE
0	46040.00
1	49920.00
2	53640.00
4	58100.00
8	61060.00
24	66420.00
67	71640.00

22

HOURS	VELOCITY
0	3091.00
1	3171.00
2	3185.60
4	3251.40
8	3295.20
24	3364.40
67	3380.20

HOURS CONDITIONED @ 110 DEG F

MUZZLE VELOCITY ~ FT/SEC

Figure 12. Muzzle Velocity Versus Conditioning Time

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As the data has the natural appearance of a logarithmic relationship, a Hewlett-Packard model 97 least squares routine was used to fit the points to a relationship of the form.

$$y = a + b \ln t$$

For velocity, selected points give

$$v = 3177 + 53.67 \ln t$$

with a correlation coefficient of .98

while for pressure the fitted constants are

$$P = 50,360 + 5096 \ln t$$

with a correlation coefficient of 0.997.

The results of this test program clearly demonstrate the very significant degradation of gun propellant performance as a function of adsorbed moisture level and prove the accuracy of the old adage "keep your powder dry".

In the future, this experimental program will be rerun to quantitatively determine the percent of moisture remaining on the grains as a function of time in the drying cycle.

SECTION V

GAMMA VALUES FOR COMBUSTION GASES

This section will provide reference values for the specific heat ratio of various gases typically found as gun propellant combustion products and also for those gases such as helium and hydrogen which are used as working fluids in light gas guns. The specific heat ratio data for oxygen, nitrogen, carbon monoxide, air, hydrogen, and carbon dioxide have largely been extracted from References 9 and 10, and the data is presented on Figures 13 to 18. The gamma values on the plots are given at 1, 10, and 100 atmospheres where $\gamma = C_\rho / C_v$.

Water vapor has reasonably curious thermodynamic behavior, and the literature is somewhat reticent in providing tabulated specific heat ratio information. Reference 11 provides data for a related parameter, the isentropic expansion exponent K which is defined as

$$K = \frac{-v}{p}\left(\frac{\partial p}{\partial v}\right)_t \frac{C_p}{C_v}$$

where, along an isentrope

$$pv^k = \text{constant}$$

The data provided for water vapor on Figure 19 is this isentropic expansion exponent.

For helium, a plot as a function of temperature and pressure is not required, in the temperature ranges encountered in light gas gun operation, and a constant value of $\gamma = 1.66$ is suitable for general interior ballistic usage.

The gamma values are important for several interior ballistic applications, particularly energy computations, in that while impetus or F_p is the value for specific energy for a propellant usually quoted, actual available total energy is:
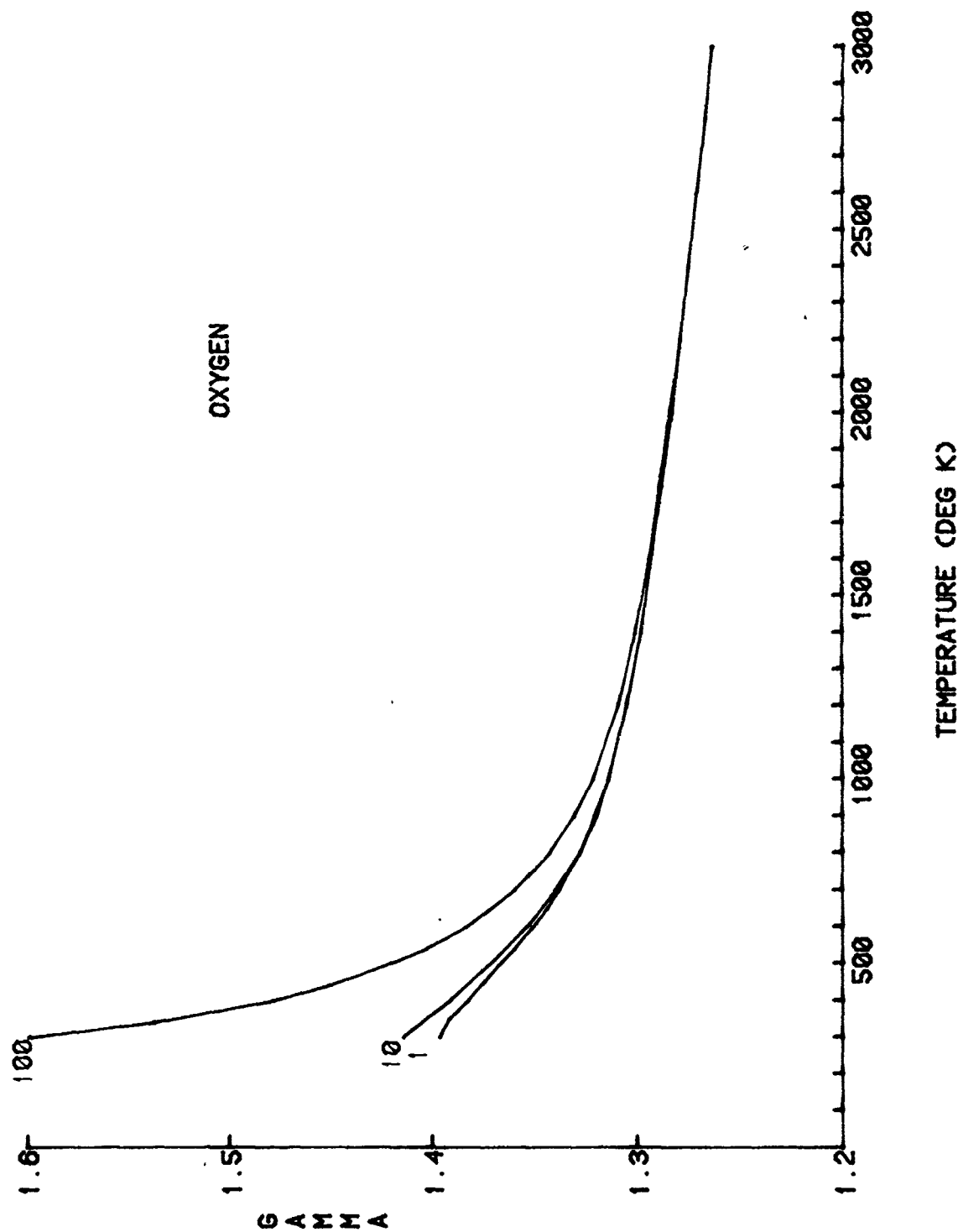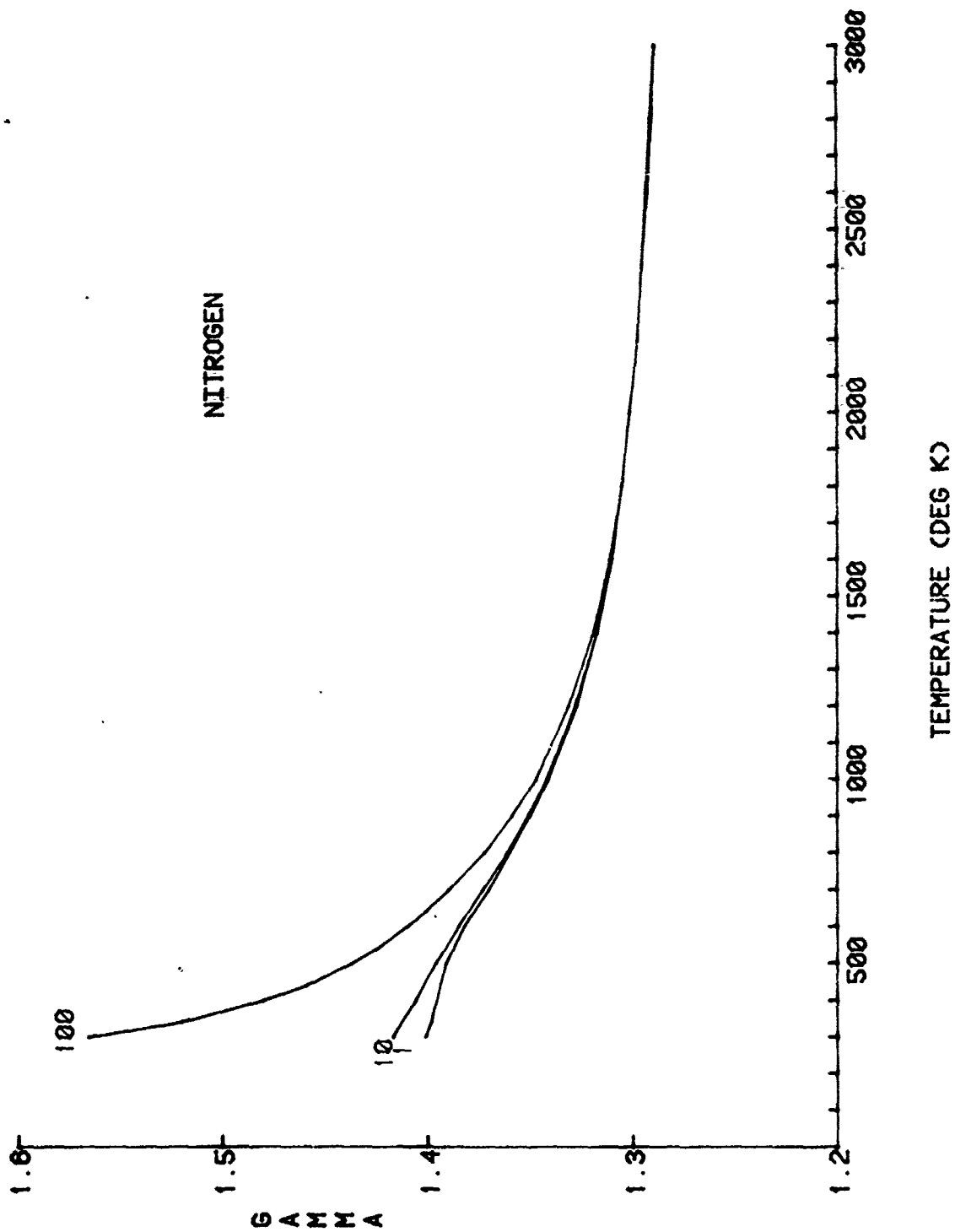
$$Q = C_w F_p / (\gamma - 1)$$

25

OXYGEN

TEMPERATURE (DEG K)

Figure 13. Specific Heat Ratio O_2

Figure 14. Specific Heat Ratio N_2
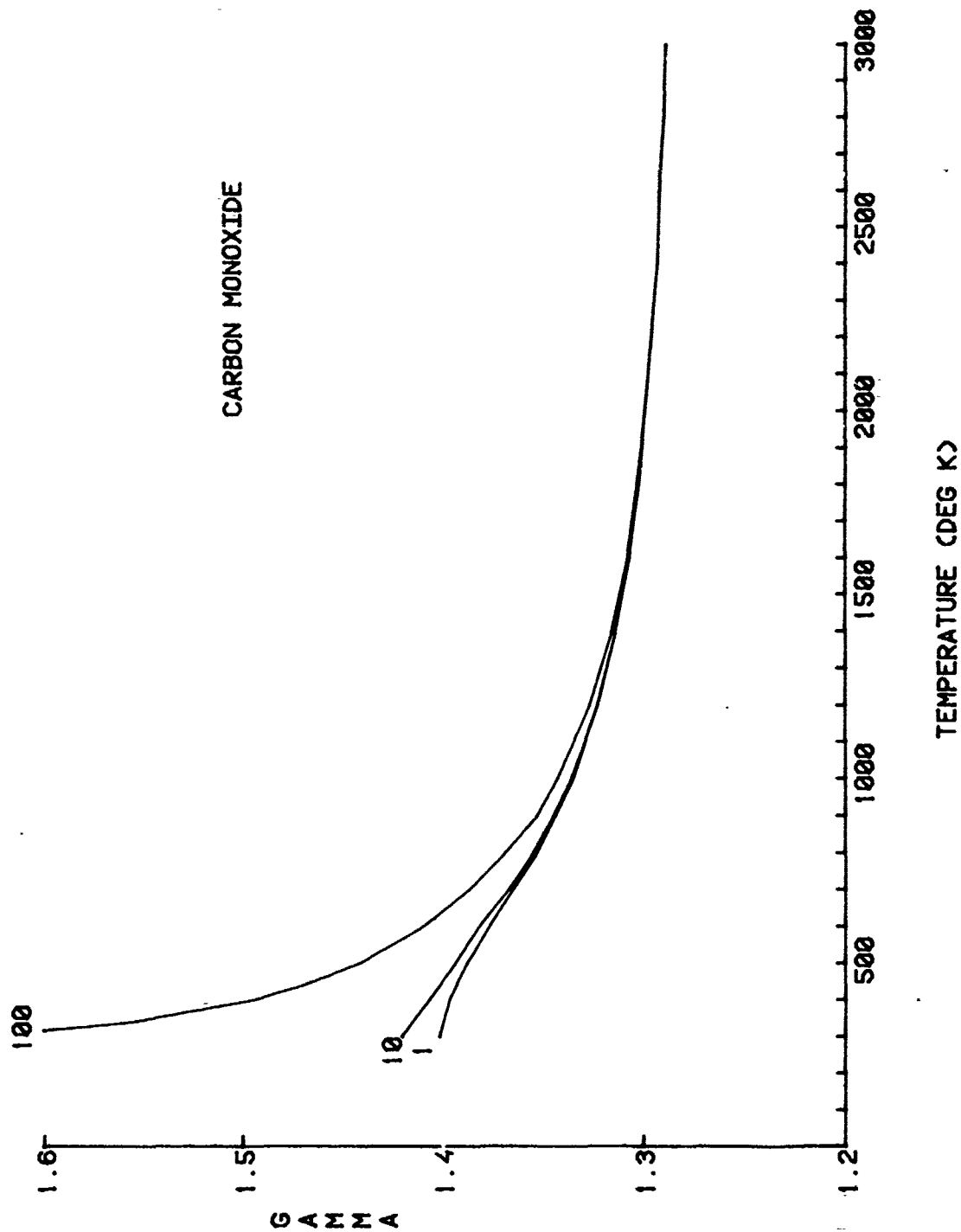
CARBON MONOXIDE

Figure 15. Specific Heat Ratio CO
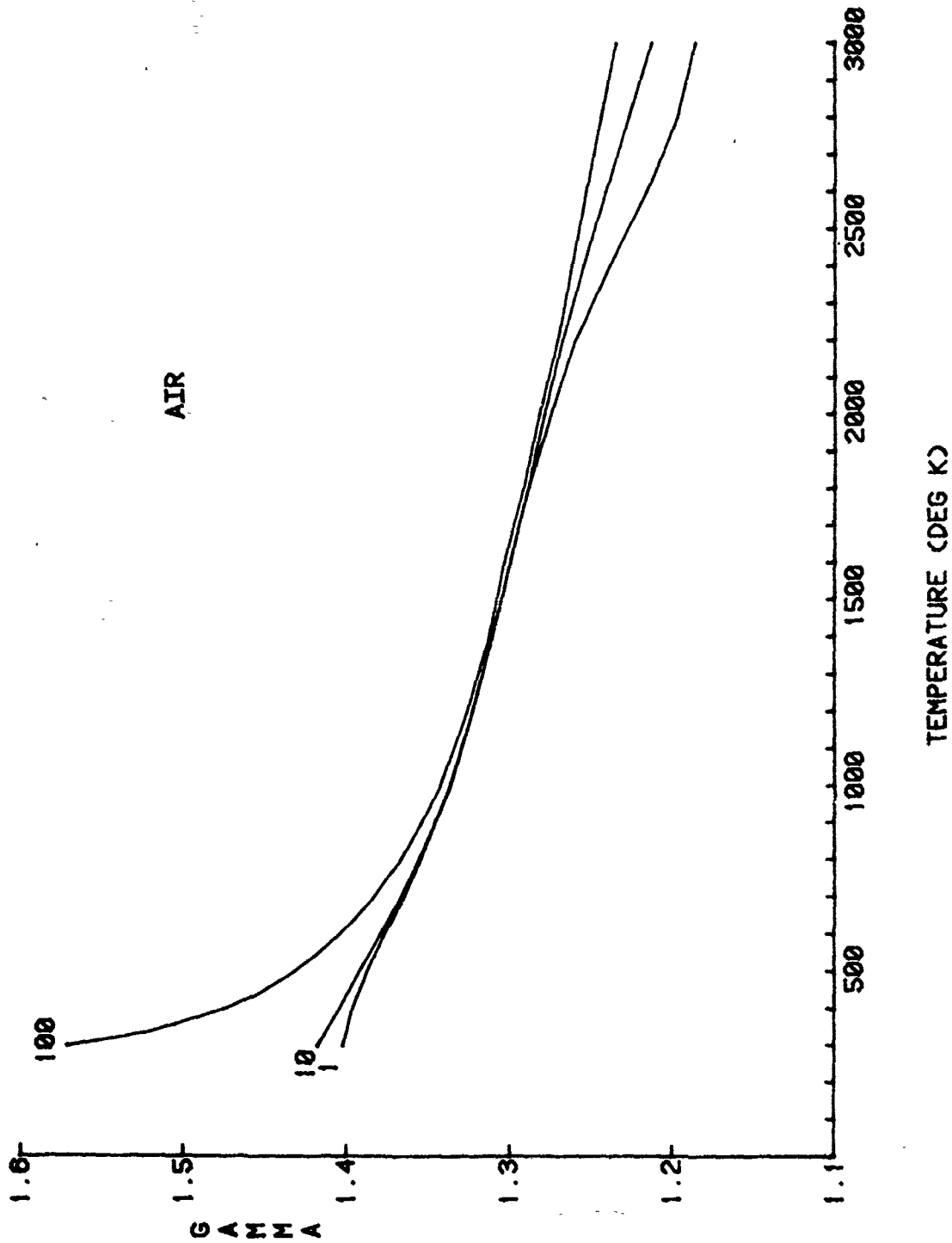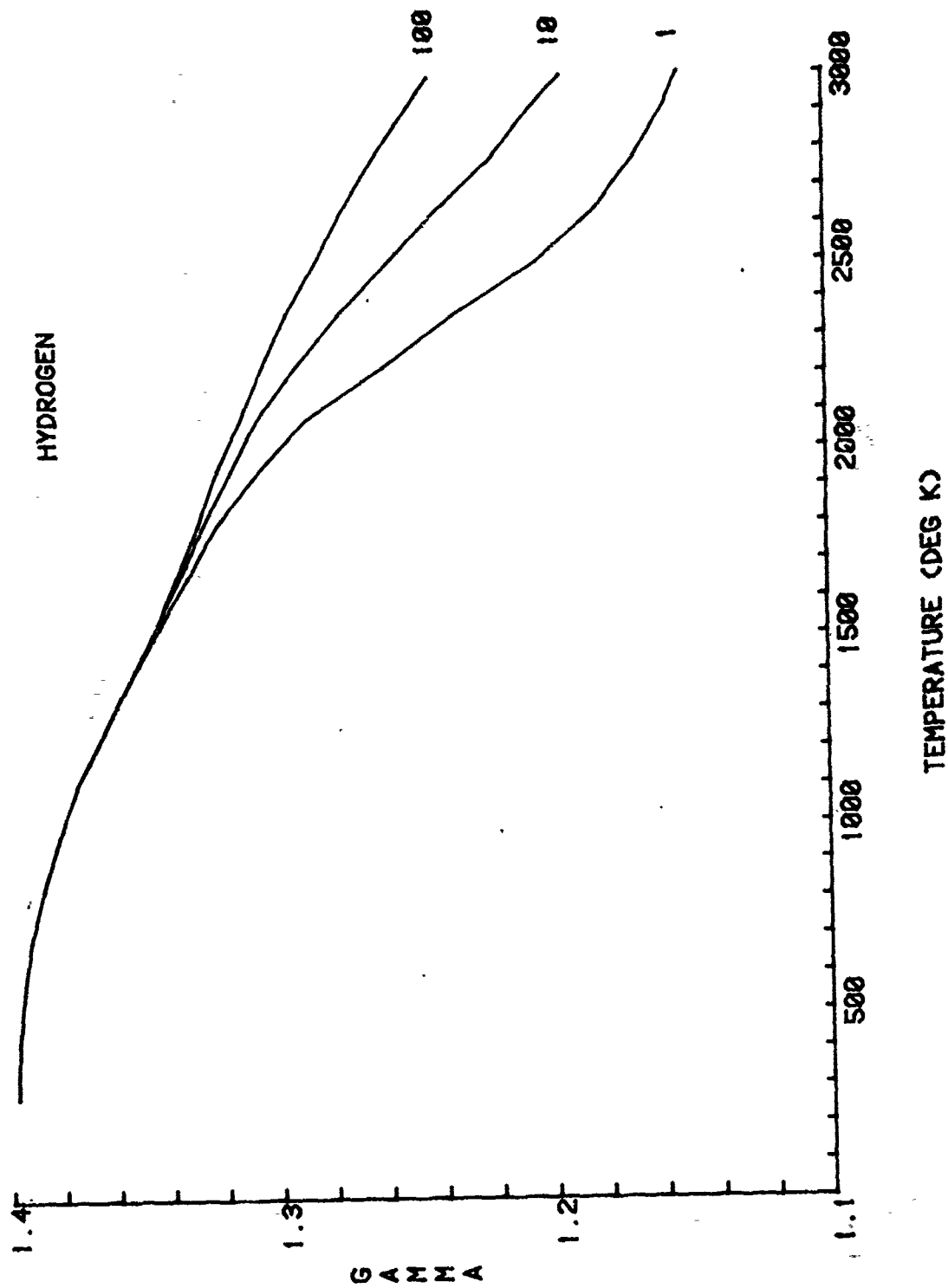
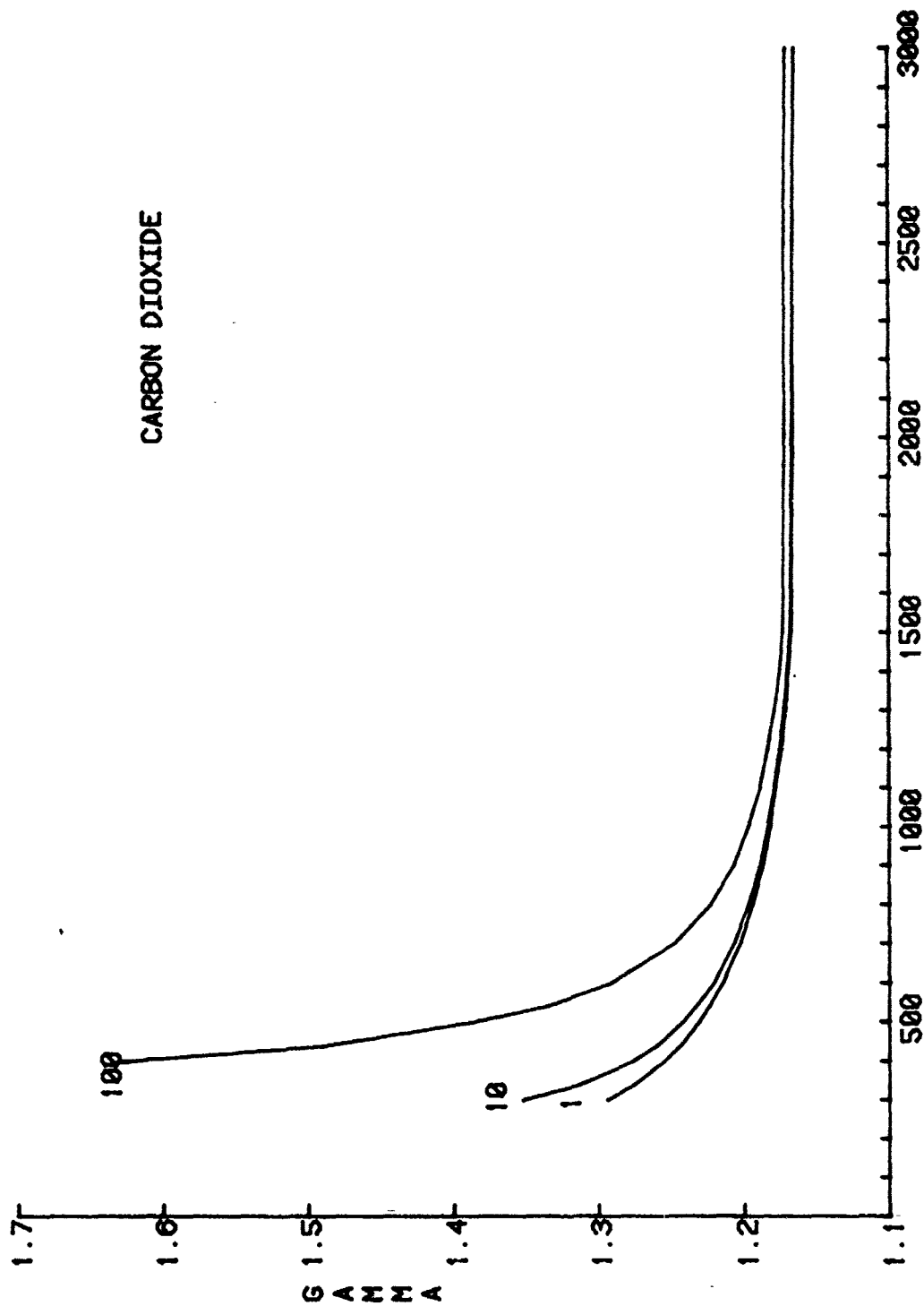Figure 16. Specific Heat Ratio Air

29

Figure 17. Specific Heat Ratio H_2
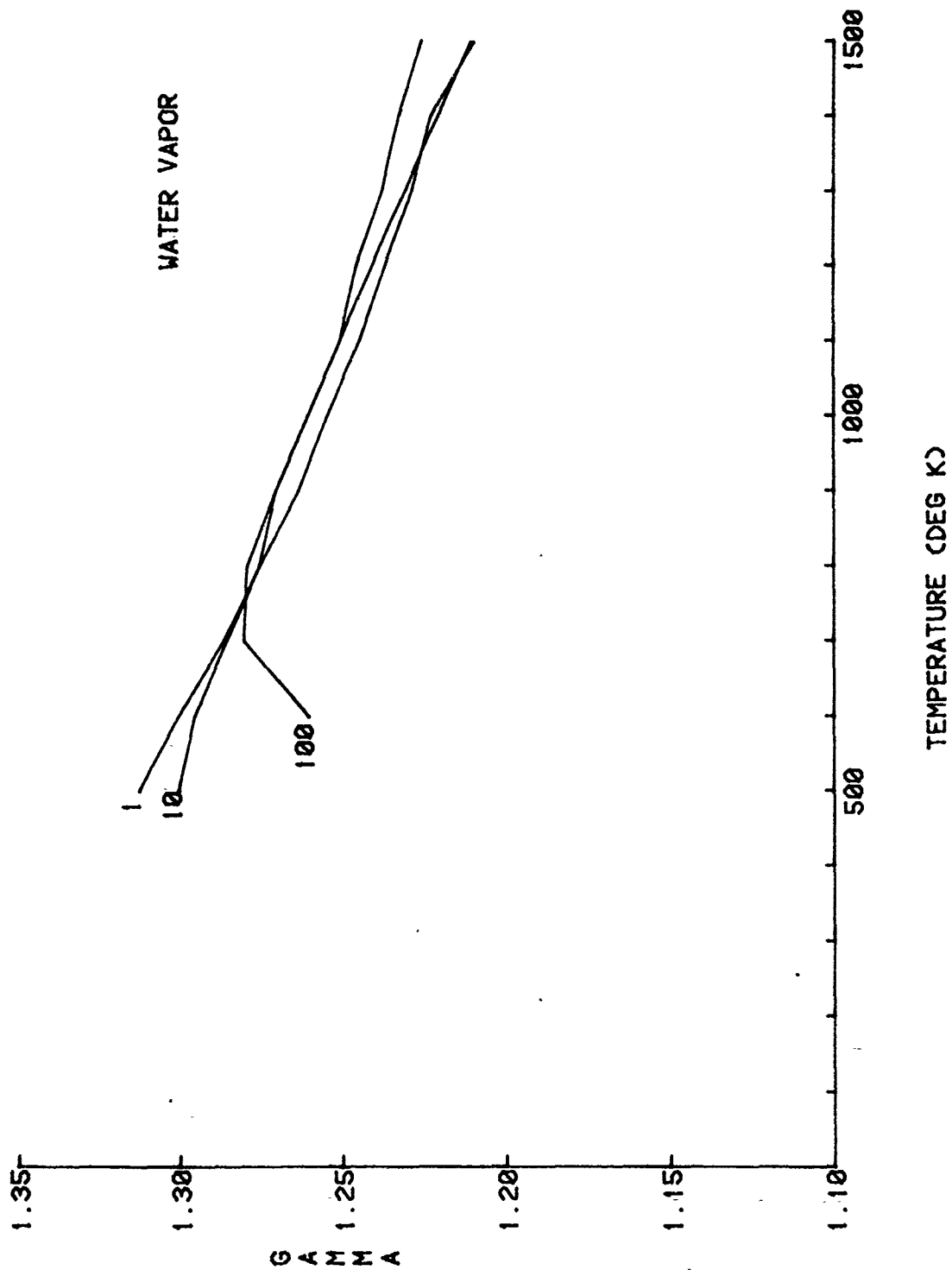
Figure 18. Specific Heat Ratio CO_2

Figure 19. Expansion Coefficient Water Vapor

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